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OIL TAGGING SYSTEM STUDY

Summary

by
RESEARCH DIVISION, ENVIRONMENTAL
AND APPLIED SCIENCES CENTER

MELPAR
An American-Standard Company
7700 Arlington Boulevard
Falls Church, Virginia 22046

for the
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
DEPARTMENT of the INTERIOR

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OIL TAGGING SYSTEM STUDY

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ABSTRACT

Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids) have been examined. Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are satisfactory for the job; and the three types of active tags reviewed show promise and merit.

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Key Words

Oil Pollution

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GENERAL

According to Federal Water Pollution Control Administration estimates, there are approximately 7000 oil spills in U.S. waters annually. This figure does not tell the whole story; the true figure may be several thousand more. The problem of oil pollution is patently serious, and grows more serious with time. One of the great problems in combatting oil pollution is to identify the pollutor: Oil pollution is illegal under at least six statutes of the U.S. Code. While small amounts of oil pollution can come from thousands of sources, a great deal of oil pollution apparently comes from a few types of sources: tankers, cargo ships and barges, offshore wells, storage tanks, and pipelines. Waterborne sources account for over half the pollution. While the problem is large, it is not infinite. There are 14,000 offshore wells, and 2,000 tankers making about 10,000 calls a year on U.S. ports. And only 400 of the tankers fly the U.S. flag. The problem is: How to identify the source of the oil discharge, cheaply and conclusively?

The most direct approach to tracing the source of pollution is to compare the slick with the oil carried by the suspect source. This approach assumes that the slick will not differ significantly from the true source.

WEATHERING OF OIL IN A MARINE ENVIRONMENT

Oil, however, is no simple compound or mixture of compounds and does not maintain its original integrity in a marine environment. Crude and fuel oils show enormous variation in chemical content, both qualitatively and quantitatively. Naturally, variations in chemical content are accompanied by variations in physical properties. Perhaps the most important event in the history of an oil slick is the evaporation of the light fractions. While the rate of evaporation will be influenced by many variables, after several days at sea the slick will consist almost entirely of compounds whose boiling point is above 370°C (approximately 700°F),[1] viz, compounds containing at least 20 carbon atoms, and probably of complex chemical structure. Most oil spilled on calm water spreads rapidly to form a film about 2 cm thick. Although many variables affect its subsequent thinning, its final thickness will be 10-100 microns on pure water, but approximately 1 mm on heavily contaminated water.[2] Thin films offer a larger surface (and hence, are more easily acted upon by the environment) than thick films.

While evaporation undoubtedly accounts for most of the volumetric loss in the slick, solution in sea water may also play a significant role. R.A. Dean[1] has argued that, while the lightest hydrocarbons have finite solubilities in water, some heavier petroleum constituents, while undoubtedly less soluble, may still go into solution, when considering huge volumes of sea water. Dean has contended that if a solubility on the order of one part per million is assumed, the whole cargo of the Torrey Canyon could have been dissolved in a patch of sea 20 miles square and 500 feet deep. In this connection, the presence of

surfactants in natural crudes (surfactants such as porphyrins and metalloporphyrins) assumes a new significance. Moreover, trace metals in petroleum are often in water-soluble form, or become water-soluble as the slick weathers.

While the slick is spreading, evaporating, and being leached of its water-soluble components, other weathering processes act upon the residue: catalytic autoxidation, photochemical oxidation, polymerization, and microbial oxidation. While it is known that oil changes its character because of oxidation, solar radiation, and microbial action, there is little information about the specific mechanisms, reaction times, and reaction products. The unsaturated, alkyl-aromatic, and alicyclic hydrocarbons in petroleum are probably oxidized to acids via peroxide, hydroperoxide, alcohol, and ketone intermediates.[3] In spite of the absorption of the shorter wavelengths of the sun's rays by the atmosphere—which reduces the ultraviolet light (UV) of less than 4000 Å to no more than 5% of the total—there remains enough energy in the residual radiation to break a variety of chemical bonds;[4] in general, aromatic hydrocarbons are more stable than aliphatic hydrocarbons to UV and visible radiation. Ellis & Wells[5] have reported that solar UV causes oils to become colored and gummy in the presence of oxygen, and that the rate of gum formation triples for every 20°F rise in temperature. Wolsky & Chapman[6] have shown that UV caused porphyrins to disintegrate rapidly in the presence of oxygen. Oil slicks are also attacked by oxidizing microflora, which are common in both fresh and salt water.[7] While many of the compounds in petroleum are undoubtedly metabolized, the metabolic pathways for large and complex hydrocarbons are not well established,[8] and the kinetics of oxidation (even for the smaller hydrocarbons) seem to be rather slow. It is well to bear in mind, however, that the species distribution of saprophytic microorganisms varies widely with latitude, and that diversified enzymatic activity is much more common in cold-water than in warm-water bacteria.[9] The question of microbial oxidation and assimilation of petroleum compounds is further complicated by the anomalous phenomena of co-oxidation and oxidation of non-assimilable substrates, which have been reviewed by McKenna & Kallio.[10]

IDENTIFICATION OF OIL SLICKS

There are two general approaches to identification, which are sometimes called active tagging and passive tagging. In passive tagging nothing is added to the oil; the slick itself must provide all the evidence for its own identification. Active tagging involves adding some known and readily identifiable material to the oil. The added material must satisfy several criteria: It must be soluble or dispersible in oil and insoluble and nondispersible in water; it must be easily detectable in extreme dilution commensurate with a high coding capability; it must be chemically and physically stable in both spilled and unspilled oil; and it must not interfere with the commercial uses of petroleum. One additional criterion: It must not be too expensive. Two figures of speech are helpful in

distinguishing active tagging from passive tagging: Passive tagging amounts to a "fingerprint," and active tagging amounts to a chemical or physical "license plate."

PASSIVE TAGGING

When oil is spilled, it may be irradiated; mixed with complicated aqueous solutions (sea water, polluted fresh water, or brackish swamp water); exposed to oxygen and air pollutants; and intimately associated with a variety of aquatic microbes; depending on local conditions, it may have been partially evaporated, emulsified, photolyzed, autoxidized, polymerized, enzymatically oxidized, and may have undergone ionic exchange. What part of the fingerprint can be stable to all these conditions? Heavy and highly branched alkanes are excellent candidates; so are the heavy and complex hydrocarbons of mixed structure that are common in lubricating oil. However, the heavy branched alkanes are (in general) exceedingly rare in oil, because the concentration of branched-chain paraffins in crude oil is a rapidly decelerating function of molecular weight.[11] The mixed-structure hydrocarbons common in lubricating oils permit an almost infinite number of structures, and the likelihood of positively identifying any one of them becomes vanishingly small.[12] After all, even though several hundred compounds have been identified in crude oil, the identified compounds "probably account for well under 50% of the constituents of a crude petroleum."[12] It should be apparent that the hydrocarbons in slicks of crude and heavy oils will contain an even higher percentage of unidentified structures. One must therefore conclude that although heavy, complex hydrocarbons are likely to be stable constituents of oil slicks, they will not serve as passive tags because they are exceedingly rare, exceedingly difficult to identify, or both.

Trace metal content (especially vanadium and nickel) and the sulfur isotopic ratios in oil have been suggested as fingerprints that could be used to identify the source of oil slicks.

Many inorganics have been reported in petroleum ash; reports of 37 inorganics were found, and the list could no doubt be extended. Many of these elements are rarely found, others are frequently found in low concentrations; only a few are frequently found in petroleum ash in concentrations above 0.1%, and, of these few, special importance attaches to vanadium and nickel.

These two metals are important because of the problems they cause industry. Like most elements of the first transition series, both are dehydrogenation catalysts (nickel is 4 to 10 times more active than vanadium), and both are commonly found in petroleum as volatile compounds. For this reason, they are often found in distillate fractions, their concentration increasing with the depth of the cut. Some of these volatile organometallic compounds alter the selectivity of cracking catalysts, increasing the

formation of coke and hydrogen and decreasing the yield of gasoline. Non-volatile vanadium, which concentrates in the residuum from which heavy fuel oil is produced, is extremely corrosive to fire-clay bricks used in furnaces; the vanadium oxides form low-melting eutectics with clay, producing hard, glassy slags that are extremely difficult to remove.[13, 14]

Both vanadium and nickel are commonly found in petroleum as compounds of widely varying molecular weight.[15] Often, these compounds are water-soluble inorganics.[16] Of the organic compounds, special importance attaches to the nickel and vanadyl metalloporphyrins because these compounds are rather stable constituents of petroleum and have great geochemical significance.[17] It is well to remember, however, that only a small fraction of nickel and vanadium in petroleum is usually found in porphyrins. While vanadyl and nickel porphyrins are rather stable compounds, they are also interfacially active and tend to concentrate at hydrocarbon-water interfaces. In light of this property, several workers have used water sprays to extract metalloporphyrins from oil; this method is thoroughly established.[16] Wolsky & Chapman[6] have also shown that when porphyrins are irradiated by UV in the presence of oxygen, they are rapidly decomposed. Furthermore, while the metalloporphyrins in oil usually have reduced side chains, oxidizing conditions usually result in poly-carboxylic porphyrin structures, which have a very marked affinity for water interfaces.[18] Indeed, Falk[19] has demonstrated an almost linear relationship between the number of carboxyl groups on a porphyrin and the porphyrin's mobility in a solvent system of lutidine and water.

In view of the fact that both the vanadium and the nickel in petroleum are often volatile and water-soluble, it is difficult to understand why they have been seriously recommended as passive tags. Nevertheless, they have been recommended off and on since 1955, if not before. Since all the recommended methods require sampling of oil slicks—which will have been partially evaporated, thereby concentrating the involatiles—it may be pointless to compare the absolute metallic contents of the slick with that of the unspilled oil. Rather, the ratio of metals (in particular, the ratio of vanadium to nickel) must be assumed constant. This may be an invalid assumption, since (in general) nickel compounds in petroleum are usually reported to be more volatile and more water-soluble than vanadium compounds. The arguments advanced for vanadium and nickel tags seem to ignore these facts:

> Vanadium and nickel are held in the oils as co-ordinated complexes with porphyrins, and are not affected by contact with sea water...[20]

or from a more recent proposal:

> The method simply entails measuring the vanadium and nickel contents of the unknown oil pollutant. There is a

> very specific amount of these metals associated with every crude -- in essence constituting an individual metallic trait. There are other chemical and physical properties for the various crudes, but these are subject to change during weathering/aging [sic]. The metallic components, however, are stable and are not affected by weathering. By simply comparing the metallic content of the spill against [sic] that of the suspected source, it is possible to limit the probable source to a specific vessel, pipeline or storage facility.[21]

Others have proposed analyzing even larger metallic suites, for example, vanadium, sodium, manganese, and cobalt; this method was proclaimed to offer:

> definite promise for the trace-element characterization matching [sic] of an actual oil-slick sample with one sample of fuel oil -- out of a number of suspect samples.... The various characterizing trace elements, occurring in the original crude oils largely as essentially non-volatile metal porphyrins, remain in the residue left when the volatile components of the crude evaporate (as from an oil slick), and when the light ends are distilled off in refining. Thus NAA [neutron activation analysis] matching of the levels of these trace elements -- between an oil slick and its polluting source -- may, for the first time, provide a method of identification of the source of oil pollution of waters that will aid in the enforcement of present oil pollution laws.[22]

While the idea of using vanadium and nickel to identify oil slicks has, at the very least, the merit of being based on some firm fact—for vanadium and nickel are very commonly found in oils, and they are often found (in small part) as metalloporphyrins, of which they are by far the two most stable[18]—these other metals, especially sodium, are very poorly advised. Sodium, for example, is common in petroleum but it is also the most common cationic metal in sea water;[23] it is therefore readily available to participate in exchange and replacement reactions with the oil slick. The petroporphyrin nucleus is an obvious target for exchange reactions with sodium ions from the sea; unfortunately, these sodium porphyrins are not very stable in the presence of other cations. Hodgson[18] and his colleagues have brilliantly summarized the evidence: It is thoroughly established that alkali metal ions in porphyrin molecules are readily replaced by other cations. They are alkali metal, large divalent metals, and finally, small divalent metals. The metalloporphyrins and complexes of porphyrins incorporating monovalent cations show rapid exchange. It has been known since the late 1940's that both the mono- and di-salts of porphyrins with

alkali metals are very unstable and break down in the presence of water. While other petroleum compounds of sodium may be more stable than sodium porphyrin, it is well to remember that one general characteristic of sodium compounds is their water solubility, and water-soluble compounds are not likely to remain in an oil slick for long.

Quite aside from the physical and chemical stability of metals in petroleum, there is the problem of distinguishing two or more samples that may be very similar. While the vanadium/nickel ratio of Kuwaiti petroleum is quite different from the corresponding ratio in Venezuelan petroleum, the U.S. does not import equal amounts of petroleum or petroleum products from these two countries. For example, about 80% of the residual fuel oil imported into the U.S. comes from Venezuela and the Netherlands Antilles, and over 90% of all the residual fuel oil that is imported by the U.S. is received in PAD District 1 (roughly, the New England, Middle Atlantic, and Southeastern States).[24] Imported residual fuel oil is far more likely to be spilled in an East Coast harbor than in a Pacific Coast harbor, and the oil is very probably a South American export. Similar considerations apply to other petroleum products. Sumatran crude oil, for example, is imported almost exclusively into the Pacific region; Venezuela and Canada together account for about two-thirds of the crude oil imported into the U.S. Exactly the same argument also applies to oil produced within the U.S. Texas, Louisiana, California, and Oklahoma together produce about 80% of U.S. crude oil; much of this oil comes from such giant fields as Wilmington, East Texas, and Kelly-Snyder. It is therefore likely that a spill of U.S. crude oil is a spill of oil from Texas, Louisiana, California, or Oklahoma, and it is quite likely that this oil came from one of the major oil fields in those states. The more specific the argument gets, the greater the likelihood becomes. For example, most of the crude oil that is processed by the great refineries of Eastern Pennsylvania and New Jersey is sent via tankers and barges from Texas and Louisiana; it therefore follows that a spill of crude oil on the Delaware River almost certainly involves Texas or Louisiana crude, and very probably involves a crude oil from one of the large oil fields in those states. How can vanadium/nickel ratios be used to distinguish one Wilmington crude from another, or one Venezuelan residual fuel oil from another? The economic realities are not especially relevant to a pure chemical argument, but in a discussion of the probability of oil spills, they should not be entirely forgotten either.

Keeping this discussion of economic realities in the back of our mind, one can proceed to the use of sulfur isotopes as passive tags. This discussion is heavily based on the work of Thode and his colleagues[25-28] at McMaster University (in Hamilton, Ontario), who have been studying sulfur-isotope ratios in a variety of geologically important materials (including petroleum) since the late 1940's. In this discussion, as in the discussion of metallic suites in petroleum, the work of scientists, whose investigations were conceived and published without oil tagging in mind, has been chosen.

Isotope fractionation is an established and important geochemical process: Oceanic carbonate is rich in O-18 with respect to ocean water, plants are enriched in C-12 with respect to atmospheric carbon dioxide, and sea sulfate is rich in S-34 with respect to the sulfur found in meteorites and basic igneous rocks. Although there are nine sulfur isotopes, only four of them (S-32, -33, -34, and -36) occur in natural sulfur; all four are stable, but they are not equally distributed: S-32 predominates (95.0%), and S-34 (4.22%) accounts for most of the remainder. The ratio of these two most common isotopes is often standardized with respect to meteorites because this ratio is virtually invariant; in the Earth's mantle, however, the content of S-34 varies by approximately 100%. The 34/32 ratio has been studied in many materials, including petroleum and sea water: In sea water the ratio is +20 ±2%, while in petroleum it varies from -8% to +33%—indeed, it varies from -8% to +28% in petroleums from Utah alone! And the apparent significance of this phenomenon has not been lost on proponents of passive tagging.

The fundamental fact in the geochemistry of sulfur isotopes is that S-34 tends to sulfate and S-32 tends to sulfide: S-32 is the more readily reduced isotope and S-34 is the more readily oxidized. 34-sulfide plus 32-sulfate tends to 32-sulfide plus 34-sulfate. In short, the heavier isotope is more readily oxidized, and the lighter isotope is more readily reduced.

While all the sulfur compounds in petroleum have not yet been identified, all the identified sulfur compounds are reduced: thiols (mercaptans), disulfides, sulfides, and thiophenes.[15] The ultimate source of this sulfur is not definitely established, but many authorities have argued that it must usually be oceanic sulfate, reduced to sulfide by such bacteria as Desulfovibrio desulfuricans; Davis[7] has summarized the evidence well. These bacteria preferentially metabolize the lighter mass isotope, viz, S-32, and it has been shown by several investigators that this preference is usually around 15%;[29] the 34/32 ratio in petroleum should therefore be about 15% lower in petroleum than in the sulfates of ancient oceans. The group at McMaster University has shown that this is usually the case. This group has shown that, while the absolute sulfur content of petroleum declines with time, the sulfur-isotope ratio stays remarkably constant. They have also shown that the content of sulfur isotopes in Devonian petroleums extending from the 49th Parallel to the Arctic is nearly constant, and have argued that the most reasonable explanation for this phenomenon is a large sea, which provided the large reservoir of sulfur of uniform isotopic content and constant oil-forming conditions. They were therefore pleased to announce that the isotope ratios in Ordovician and Silurian oil of Texas and Ontario, although separated by several thousand miles, were quite similar.

What is the conclusion to be drawn from this evidence? It is, quite simply, that S-isotope ratios are just another general index of geological age. Geochemists have several such indices (e.g., ratio of complex cyclic structures

to simple chain structures, not to mention radiocarbon dating). It is difficult to see, however, how any such index can be of much use in identifying oil spills. For example, the United States' largest foreign source of oil (Venezuela) is a major shipper of Tertiary crude; so is Louisiana, the second most productive oil state. The second largest foreign source of oil (Canada) sends large quantities of pre-Mississippian crude to U.S. East Coast refineries; so does Texas, the largest oil-producing state. Miocene oil is common in Louisiana; it is also common in Indonesia. Are S-isotope ratios sufficiently precise to distinguish Miocene from Eocene? —if not, oil from Fresno, California, cannot be distinguished from the oil of Sanga Sanga, Borneo, or Plaquemines Parish, Louisiana.[24,30]

There is another objective, however, that may be even more important. The sulfur in oil is reduced, but when oil is spilled at sea, the sulfur is put in an oxidizing environment. Because of kinetic isotope fractionation, the S-34 will be more readily oxidized than the S-32, other things being equal. The logic of this process leads to the conclusion that the more the spill is oxidized, the lower the 34/32 ratio will be; a week-old oil spill should have a lower isotope ratio than a day-old spill from the same source. If the fractionation effect were strong enough, the delta-value might go from highly positive to very negative. This combination of geochemical fact, oxidation kinetics, and petroleum-trade statistics leads to the conclusion that sulfur-isotope ratios could not very well be used to prove a violation of oil-pollution laws.

SPECIAL CASES OF PASSIVE TAGGING

While no easily identified passive tag that is unaffected by marine environments is known, several kinds of passive tags can be used profitably as presumptive tests on the identity of oil spills under special conditions. In general, the requirements on passive tags should not be different from the requirements on active tags: Both kinds of tags should be unchanged by weathering and microbial oxidation, soluble or dispersible in oil, insoluble and nondispersible in water, and involatile. However, there are special circumstances in which some of the requirements on passive tags may be relaxed. Where oil pollution is infrequent, where there are few possible sources of pollution, and where weathering may be assumed to be inconsequential or insignificant (because of the slick's freshness), several methods of chemical analysis—such as spectrophotometry, gas chromotography, fractional distillation, pyrolysis, mass spectrometry, and comprehensive physical measurement, i.e., density, viscosity, and refractive index—supplemented by other independent evidence—may identify oil slicks by passive tags in the spilled oil. Chemical analysis is useful when it does not have to bear the whole burden of proof. A combination of analytical techniques (such as gas-liquid chromatography, controlled pyrolysis, mass spectrometry, and computer calculations) cannot be relied upon to yield a "fingerprint" of the slick.[31] If the spill has not been extensively weathered and if there are not many possible sources of pollution, the combination of analytical techniques

is wasteful: Where other independent evidence is convincing, extensive chemical analysis is not required. However, where there are many possible sources of pollution, where pollution is frequent, and where the spill may have been weathered for days or weeks (or mixed with other spills, some of which may have been weathered), it seems highly improbable that any combination of analytical techniques could stand up in court to a carefully reasoned chemical defense.

The problem of mixed and continuous pollution is not unknown. According to Ludwig and his colleagues,[32,33] the beaches in Southern California are commonly polluted by a mixture of oil and asphalt from natural seepage, liberally supplemented by tanker and drilling wastes. Similar conditions frequently pertain along the Gulf Coast. A senior scientist at the Woods Hole Oceanographic Institution was recently reported[34] to have said that he could not sail anywhere in the Atlantic—even a thousand miles from land—without finding oil. The methods discussed cannot be recommended for such areas as Southern California, nor for areas that are frequently afflicted with oil pollution.

To begin, all the methods of passive tagging already discussed can be used (although they are more expensive than several other methods) as long as there is plenty of independent evidence that the oil slicks are fresh and have not been mixed with other oil pollution. Other simpler methods of identification were published in the U.S. and England in the early 1950's; these methods make use of the simple techniques of paper chromatography which will be used as an example in the following paragraphs.

Schuldiner[35] reported (in 1951) a simple method of spot chromatography that had produced evidence for prosecuting and convicting oil polluters in Baltimore, Maryland, and the upper Chesapeake Bay area. He sampled the oil slick, then boarded suspected ships and sampled bunker fuel oils, bilges, loose oil on the decks or sides of the vessel, on fuel intake valves, and on adjacent docks. The samples from the slick and the ship were strictly treated as comparison samples. Small spots of the samples were applied to blotting paper, allowed to develop completely (i.e., to stop spreading), and were then examined under ordinary and UV illumination. He found that various crude, semi-refined, and refined petroleum products gave characteristic spot chromatograms, and that the chromatograms from known crudes invariably gave identical radial fluorescence patterns. While Schuldiner's chromatograms can be effective, they are not perfect: They entail at least three troublesome problems. First, confluent multiple spills will give chromatograms that are characteristic of the mixture, not of the components of the pollution; it is very doubtful that the chemical mixture can be resolved into its legal components, or that a given slick can be proved not to be a mixture unless the circumstantial evidence is overwhelming. (This objection applies with equal force to all other methods of passive tagging.) Second, any but the freshest slicks may have become viscous and emulsified, may have experienced considerable evaporation, and their asphaltenes and other heavy components may have agglutinated into a discrete particulate phase;[36] the

chromatograms of the slick and the source are likely to differ unless the slick is fresh, and the size of the difference will largely depend on the slick's age. Moreover, if the slick is very viscous or emulsified, it will have to be filtered, extracted, heated, and/or dissolved in a non-fluorescing solvent in order to be chromatogrammed; while this treatment may not be damaging, it is not helpful to the prosecution's case either. Third, it is not an unmixed blessing that identical chromatograms are invariably produced by crudes from a given area. If all (or even many) Venezuelan crudes give identical chromatograms, and if two or more tankers carrying Venezuelan crude have recently been in the area of a spill, it is not clear how one ship rather than the other could be blamed.

Another simple chromatographic method (this time, paper-strip chromatography) was independently published in 1953 by Herd,[37] who claimed that he had used this method to identify fuel oil that had been spilled in the harbor of Wellington, New Zealand. While Herd was apparently ignorant of Schuldiner's work (in any event, he did not cite it), his claims are strikingly similar, and he asserted that his method "gives visual evidence of complete identity or of non-identity and, if necessary, the strips can be used as evidence in a court of law." All the reservations that apply to Schuldiner's methods apply just as strongly to Herd's. One further reservation merits special attention: Herd's methods "identify" only the ether-soluble portion of the slick. Although the ether-insoluble fraction of a slick is admittedly difficult to work with in the analytical laboratory, it can provide valuable information (particularly on naturally occurring microsolids); in any event, it does not seem prudent to ignore it altogether because it can be a sizable fraction of the slick. Ludwig & Carter[32] have reported that 12 crude oils contained (on the average) 7.9% ether-insoluble material, that some crudes contained as much as 15.5% ether-insolubles, and that one film of oil collected at a beach near Santa Barbara contained 6.5% ether-insolubles.

ACTIVE TAGGING

There are reasons to have serious reservations about the validity and efficacy of passive tagging. Identification based on passive characteristics seems to be especially worrisome because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized at sea; furthermore, even if these processes do not occur, they create formidable forensic problems for the prosecution, and telling counter-arguments for the defense.

If the intrinsic components of the oil slick do not lend themselves to reliable identification, the possibility of introducing additives (active tags) that will suit the purposes must be considered. What is required of an active tag? Ideally, it should satisfy ten criteria.

1. It must be an unusual material that is never found in the natural environment and is found only in the petroleum to which it has been added.

2. It must be compatible with (i.e., chemically unreactive and physically stable) and soluble or dispersible in the oil.

3. It must be both insoluble and nondispersible in water.

4. It must be relatively involatile.

5. It must be stable to chemical, photochemical, and microbial degradation in the oil-slick environment.

6. It must be easily detectable in extremely small quantities by readily available analytical techniques.

7. It must have the ability to be modified so that the material can be coded, and when added to a particular oil shipment provide a unique code or "license plate" for that carrier or transporter.

8. It must remain with the oil during the course of its history following a spill.

9. It must in no way interfere with the end-use applications for that oil, nor complicate further processing and refining.

10. It must be available in quantity at economical prices.

While few tags will be ideal, many candidate tags will satisfy these criteria to some degree.

Although many types of tags have been investigated, there are two types of oil-soluble tags and particulate tags that have merit. The problem of radioactive tags has also been considered.

HALOGENATED AROMATICS

Over the past several decades, many studies have been performed to identify and characterize the constituents of petroleum. Although many types of aliphatic, aromatic, and heterocyclic compounds have been identified, there is no evidence of halogenated, polynuclear aromatics in crude oils. This class of compounds has many other characteristics that are worthy of attention.

First, polynuclear hydrocarbons are (in comparison with aliphatic hydrocarbons) quite stable to oxidation.[38] This stability is due, in part, to the resonance and bond-dissociation energies of the aromatic system, whose

resonance energies increase markedly as the number of condensed rings increases.[39] Halogenation of aromatic rings has, in common with nitration, sulfonation, and acylation, the great advantage of stabilizing the ring against further attack;[40] it also increases the involatility of the parent hydrocarbon, but (in general) does not affect water-insolubility or oil-solubility.

An important feature of halogenated polynuclear aromatics is that there are many different ways to substitute F, Cl, Br, or I (or their combinations) on condensed aromatic nuclei, thereby providing a large number of specific tagging compounds. Moreover, there are many isomers of each parent hydrocarbon. Depending on the parent hydrocarbon, a large number of mono-, di-, and polysubstituted isomers can be produced with halogens, singly or, a fortiori, in combination. The simplest possible example, naphthalene, has two products of monosubstitution ($C_{10}H_7X$), ten products of monosubstitution ($C_{10}H_7X$), ten products of disubstitution ($C_{10}H_6X_2$), and 14 of the mixed type ($C_{10}H_6XY$), where X and Y are any two halogens. There are 42 known and fully identified polychloronaphthalenes; it is obvious that larger condensed systems (say of six or more rings) offer even more structural isomers for selective halogenation. Even the monochloronaphthalenes have boiling points above 250°C (482°F), and further halogenation raises the boiling point correspondingly; the vapor pressures similarly decline with increasing polycyclic condensation. The stability of overcrowded halogen compounds (e.g., octachloronaphthalene) has also been demonstrated.[41] In view of the various polycyclic nuclei (and the several structural arrangements that are possible for each) that may be halogenated, and the numerous possibilities for halogenation (involving single or several halogens), it is clear that a large family of coded compounds that can be readily distinguished from natural petroleum compounds can be synthesized.

It is important for active tags to be identifiable in the slick even after long exposure to the elements and weathering, which ordinarily increases the concentration of asphaltenes in the slick. Petroleum asphaltenes are polycyclic, comprising mostly aromatic rings[42] in a pericondensed sheet configuration.[43] In general, these asphaltenes might present a considerable background problem. However, the analytical technique suggested for the detection of halogenated active tags should minimize this problem, viz, gas chromatography using an electron-capture detector.

The electron-capture detector is a substance-specific device that is sensitive to certain types of molecules containing electrophilic atoms or groups (e.g., halogens, carbonyls, nitro groups, etc.) and certain condensed-ring aromatics, metals, and the like.[44-53] It has a very low sensitivity for hydrocarbons other than aromatics.[54] Furthermore (and very important), the detector is extremely sensitive to halogen substituents: It can reliably detect halogenated hydrocarbons in quantities as low as 10^{-4} to 10^{-6} ppm;[55] under optimized conditions, a projected sensitivity of 10^{-10} ppm has been reported.[44]

Electron-capture gas chromatography has been used successfully to determine parts-per-billion concentrations of chlorinated insecticides in waste water samples,[56,57] and chlorinated hydrocarbons in air samples.[58] Since gas chromatography has been used extensively to separate and characterize the components of petroleum and its products,[59,60] it can be used with reliability and precision to separate the components of an oil-spill sample. Coupled with the extreme sensitivity afforded by the electron-capture detector, gas chromatography can be used to ascertain the presence of an active tag by virtue of the tag's structure and substituents. Detection and identification of the tag can be expedited by reference to a catalog of retention times of the several tagging compounds on a standardized chromatographic column. When an oil sample is brought in for analysis, the retention times of the various chromatographic peaks of the sample can quickly be compared with the catalog, and the proper component peaks identified. The correlation between chemical structure and column retention times (or elution values) is well documented.[61,62] Halogenated aliphatics,[63,64] heterocyclic compounds, and unhalogenated polynuclear aromatics (as well as inorganic halogens) should not interfere because their retention times (and their detectability by the electron-capture device) will not correspond to the tag's behavior. However, if several peaks should occur near (or overlap) the tag's peak, these particular fractions can be collected and rechromatographed under operating conditions that will give a better separation.

Although nothing is known experimentally about the stability of halogenated polycycles in an oil-spill environment, there are excellent theoretical reasons for believing that these compounds will be stable. In general, aromatic structures are stable to oxidation at ambient temperatures and pressures; halogenation further protects the aromatic nucleus from chemical attack. There are excellent grounds for believing that halogenated tags will be much less reactive than the rather inert condensed aromatics that are naturally present in oil, often in large quantities. Since condensed aromatic compounds are not easily attacked by microorganisms, and since halogenated aromatics are even more stable than the corresponding parent hydrocarbons, there is also excellent reason for believing that the tags will be stable to microbial attack. All of this, however, is theoretical conjecture, not proven experimental fact.

Because of the great sensitivity of the electron-capture detector to halogenated compounds, it should be evident that very little of the tagging material is required to tag a large volume of oil. For example, the largest tankers now on the drawing board will hold 500,000 tons of oil. How much tag must be added to identify such immense cargoes? The theoretical limit of detection by electron-capture gas chromatography is 10^{-12}. Therefore, 0.016 ounce of tag is (theoretically) sufficient, if properly mixed, to tag a half million tons of oil. But why push the limit of detectability? Why not allow a safety factor of three orders of magnitude? Why not, indeed, because then only 1 pound of tag (about 1 pint) will safely do the job. And "safely" is very safe: One gram of oil slick

(about 1/4 ounce) will contain one nanogram of tag, and one nanogram of a halogenated aromatic substance is extremely easy to detect by electron-capture gas chromatography.

It is not without interest that electron-capture gas chromatography is several orders of magnitude more sensitive than emission spectroscopy[65] and approximately two to three orders of magnitude more sensitive than ordinary neutron-activation analysis[66, 67] (i.e., activation that does not use very fast neutron fluxes). By combining gas chromatography with mass spectroscopy, the tags can be absolutely identified.[68, 69] Just as important, because of the sensitivity of the electron-capture detector, the tag can be used in extreme dilution, and can therefore be added to the oil in amounts which will not interfere with further processing or uses of the oil.

ORGANOMETALLICS

Halogenated aromatic molecules are not the only attractive class of oil-soluble tags. In 1962, a group at the National Bureau of Standards,[70] in collaboration with the American Petroleum Institute, developed a number of stable, oil-soluble organic compounds (mostly organometallics) for use as analytical standards in the spectrographic analysis of petroleum products. The trace elements include Al, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, P, K, Si, Ag, Na, Sr, Sn, V, and Zn; as cyclohexanebutyrates and/or ethylhexanoates, these metals make spectrographic standards that have the following properties: Each is reproducible, stable, nonvolatile, oil-soluble, and compatible with all the other spectrographic standards in this series. Many of these metals can be detected spectrographically in extreme dilution (parts per million or less), so that one gram could be used to tag a ton or more of petroleum. The 28 compounds that were selected as standards were chosen from an initial list of over 150 candidates; many of the candidates that were rejected as spectrographic standards may still be useful as active tags for oil spills: One of the principal reasons for rejection was extreme chemical purity (e.g., the metal naphthenates), and this requirement might be somewhat relaxed for oil-spill tags. These 28 standard samples, prepared in solid form for easy weighing and handling, may be purchased for $2.00 a gram from the National Bureau of Standards. Obviously, in mass production (with some relaxation of the requirements for extreme chemical purity), the price might be significantly reduced.

Even though all this work on spectrographic standards has made the use of certain organometallics an attractive possibility, there are still several problems and doubts that must be resolved. First among these is the problem of solubility. Only a few of the Bureau of Standard's organometallic standards could be dissolved in oil, without heat or other solvents. If the standard were dissolved in a solubilizing agent (such as a free carboxylic acid, a diketone, or an ester) and then diluted with the base oil, however, the resultant solutions had optimum stability and highest concentrations of trace metal. The solutions were

judged satisfactorily stable if a solution of at least 500 ppm of the trace metal of interest remained "clear and devoid of visible change during several weeks at room temperature." An excellent solubilizer and stabilizer was found to be an equimolar mixture of bis (2-ethylhexyl)amine and bis(2-ethylhexyl)dithiocarbamic acid in an equal volume of xylene. It is not clear, however, what the highest stable concentration of metals might be. A related question is more important still: What happens to the analytical standard once the solubilizers and stabilizers have evaporated, as is likely after a slick has aged on the sea for several days? Will the standards gel or precipitate?

A second major problem is background: Most crude oils contain traces of inorganics (especially metals), and some crudes have more than 0.5% ash; there are several excellent reviews of the literature on this topic.[13, 14] Many refined petroleum products also contain metals, either deliberately added (e.g., components of additives to impede corrosion and oxidation or to improve lubricating properties), or adventitiously present (e.g., volatile organometallics in the crude that were not removed during refining). How can this background be distinguished from the active tag? Analysis of petroleum shipments for the presence of background interferents is obviously not the answer: — It is much too costly, for one thing, and for another there is no guarantee that the metallic suites in the oil slicks will be identical to those in the unspilled oil. Indeed, there is every reason to believe that the suites will be drastically different.

A better solution is to separate the tag from the slick (by chromatography, for example) before attempting further identification. Since the tag is a chemically stable "known," and since the organic moiety of the tag (e.g., cyclohexanebutyrate) should be rare in petroleum, there is no reason to believe that background suites will invalidate this method of tagging. However, separating and concentrating the tag from each slick sample adds to the time and cost of identification; since there are several thousand oil spills in U.S. waters each year, the problem of time and cost is not inconsiderable.

RADIOACTIVE TAGS

Radioactive isotopes have been examined for possible use in a tagging system, and eliminated for two broad reasons. First, there are not enough isotopes with the right half-life to make the system work and second the use of radioactive material in public places is objectionable for fear of contamination.

Ideally, a radioactive tag has a lifetime of 90 days, a reasonable cost, is easily detected, and readily available. Lifetime of all tags should be about the same so that the relative abundance of isotopes does not vary with time. Thus, a minimum tagging system would have 30 or more tags available with half-lives between 70 and 110 days. Of 1700 isotopes examined, 15 have half-lives of 70 to 110 days and, of the 15, a majority were either too expensive or too difficult to detect.

Politically it is not wise to put radioactive material in oil when there is any possibility that the radioactive material might escape into the air or water. Recent experiences in Japan with the visit of nuclear submarines show how sensitive the public is about radioactive contamination of water.

PARTICULATE TAGS

Before discussing active particulate tags, it is well to say a little about the particulate material that is naturally found in petroleum. The basic reference on this subject is a 1937 paper by J. M. Sanders,[71] to whom all more recent researchers are heavily indebted. In general, the particulate matter in petroleum consists of spores, pollens, fragments of tissue, hairs, microalgae, bits of feathers, etc. In addition, much of the particulate matter is in the form of asphaltenes, which are identified as suspended solids, colloidal particles, or solute molecules, depending on the investigator and his techniques.[43] Although these particles can convey a wealth of information to the careful investigator, their relatively small number and wide variety prohibit their use as particulate passive tags; furthermore, an oil spill may entrain pollens, spores, and other biological matter during its exposure to the elements.[72]

Adding well-characterized particles to oils is a promising technique. In the first place, these particles can be easily manufactured under current technology; second, they can be added to oil in small, measured quantities; third, there is good evidence that, if the need arises, they can be isolated from the oil matrix in quantities sufficient for very specific identification. Active particulate tags share all the advantages of active oil-soluble tags (viz, specificity and small amounts of tag for proper identification), and offer several other advantages that might make them more suitable. Foremost among these advantages is the ease with which such particles may be produced by one basic technique: grinding and spheroidizing of solids produced from an appropriate liquid melt.

Rather homogeneous solid material can be obtained by (1) solidification of a liquid melt, (2) coprecipitation from solution, (3) efficient mixing and sintering of suitable solids, and (4) deposition from a vapor phase; almost any such material may then be spheroidized. It is recommended that particulate tags be prepared as microspheroids for several reasons: (1) Their small surface area per unit volume and lack of areas of large surface curvature make them relatively insusceptible to chemical reactions; (2) these same qualities make it rather unlikely that they will clog or impact upon passage through small apertures, or adhere to interfaces; (3) microspheroids are much more readily sized (e.g., by sieving, sedimentation, and microscopic methods) than any other shape; and (4) the technology for producing them is eminently feasible, and so is the technology for characterizing them. The flowability of microspheroids makes them ideal for unit operations where mixing is necessarily of importance; flowability is obviously important where trace solids are to be added to a very large amount of liquid. All these points also apply to simplifying the preconcentration and

isolation required in any analysis of suspensoids. Finally, small particles (10-50 microns) are not rare in nature; but very smooth microspheroids of this size are much less common.

The most common process for making microspheroids is liquefaction of a particle followed by solidification in a dilute, slowly moving gaseous "suspension." Other common techniques are: tabling to produce Lucite spheroids; deposition from liquid solution for certain resins; and mechanical action, as when polishing compounds used in ball mills produce ceramic or glass spheres. There are also several methods for making microspheroids from metals.

Many materials have been made into microspheroids: soft and hard glasses[73-75] (which may be "doped" with a wide variety of metallic salts), metals,[76,77] ceramics, nitrides, carbides, celluloses, starches, polystyrene, phenolic resins, and many other organics.[78] Many suitable microspheroids are already commercially available; others can be expeditiously made by custom synthesis. Their costs range from a fraction of a cent a pound (for some commercially available materials) to $1,000 a pound (for custom synthesized rare metal microspheroids).

Exact methods for analysis and identification of oil spills that contain particulate tags depend on many factors. A thumbnail sketch of what, at this time, appears to be a reasonable procedure follows:

a. Microspheroids of about 10 microns diameter would be produced by spheroidizing a suitable, finely ground and sized solid.

b. These particles would be characterized in preliminary tests to ensure proper quality control over such critical factors as particle diameter, density, content of trace additives, etc.; the data would then be carefully cataloged.

c. The particles would then be metered into the specified petroleum (preferably as it passes through a pipeline or as it is pumped into a tanker). In order to have, on the average, 10^3 particles per liter of oil, only about 5×10^{-4} gram of particles needs to be added to each ton of oil; this amounts to 50 grams for a 100,000-ton tanker.

d. Upon spillage, a representative sample would be taken from the slick; the sample need not be much more than a few liters.

e. The particles in about a liter of spilled oil would then be preconcentrated as follows: (1) centrifugation and washing with a light hydrocarbon, (2) washing with more digestive liquids (perhaps acids or bases), (3) a terminal filtration and wash on a Millipore filter, and (4) transfer of the solids to suitable microscopic mounts.

f. Analysis (as in step b.) to identify the particles. These tests might include microscopy (for size and shape, color, phosphoresence, fluorescence), microanalysis (for density, hardness, trace analysis), or microspectrometry (light absorption, fluorimetry, reflectance). Microspectrofluorimetry could provide a characteristic spectrograph of just one or of a number of particles; such a trace would, indeed, be a "fingerprint."

g. The data from the preceding step would be compared with the data catalog (see step b.).

h. In the case of a multiple, confluent spill, the individual offenders could be identified readily, provided that only one type of tag had been added to each oil. To determine how much of the spill was due to each offender would involve characterizing a larger, representative sample of microparticles; based on the number density of each type of tag, proportional liabilities could be estimated.

Microspheroidal tags permit of a very large number of identifiable forms. Considering only particle sizes of 10-50 microns with an error of ±2.0 microns for a given size, there are at least 11 distinct and well-defined sizes.[79] For density, given a range of 0.9 - 1.50 grams/ml and an error of ±2%, we have, again, at least 11 possible characterizations.[80] The product of 11 sizes and 11 densities is 121 distinct particle types. In addition to these types, particles may contain trace amounts of chemically detectable materials, which may be characterized qualitatively or quantitatively. A series of microtests could easily determine whether or not 20 or so readily identifiable trace chemicals are present in the particle.[81-85] With a very simple binary code (in which each of the trace chemicals is merely determined as "present" or absent"), 20 trace chemicals permits 2^{20} (1,048,576) possible particle characterizations. In combination with the 121 basic particle types, trace-chemical binary coding gives well over 100 million types of identifiable particulate tags.

ADDITION OF ACTIVE TAGS TO PETROLEUM

The metering of small amounts of liquids has been developed by the chemical, pharmaceutical, and processing industries; ideally, the tags would be injected into the oil as it passes through a pipeline or as it is pumped into a tanker). For the particulate tags we recommend (2-50 micron spheroids), the same techniques will suffice. Addition of a tracer material to petroleum involves two similar and related criteria: First, the tracer should be in a homogeneous phase, and, second, this carrier phase should be injected uniformly into the petroleum so that the resulting tagged dispersion (or solution) is also uniform. There is ample evidence that relatively stable dispersions of particles in a petroleum-based liquid are easily produced. It is important that this stability be maintained when the carrier fluid is injected into the petroleum. Surfactants are critical to stability.[86] In crude oil, enough surfactants (such as

porphyrins) are usually present to assure stability (at least for the dilute suspensions being considered); in refined products, it may be necessary to select the particulate tag with great care so that the appropriate surface properties (hydrophobicity and oleophilicity) pertain. Highly polar materials (e.g., ionic salts) actually stabilize suspensions when the particles are larger than about 1 micron; the only important exceptions are metal sols, which, however, are stabilized by organometallic molecules.

According to Koelmans, "...a [disperse] system is stable when a crossing of the potential barrier between the particles by thermal motion alone is very improbable";[87] this potential barrier is about 15 kT for a modestly charged double-layer and is much greater than the usual thermal energies (about 1 kT). This energy difference also applies to particles approaching an interface: Thermal energies cannot overcome the surface potential barrier. Very concentrated suspensions (20-90 weight %) may be stabilized by adding small quantities of dissimilar particles;[88] this stabilization technique may be of value in prescribing carrier suspensions.

Once a stable carrier suspension has been produced, it can be metered into petroleum without further problems. Many metering pumps are available at nominal cost; some of these (through mechanical action on a disposable diaphragm, bladder, or flexible tube) do not even contact the metered fluid. Since the volume of the metered suspension or solution may be increased almost at will, pump capacities are not of special importance. Sufficiently stable particle suspensions can be produced and then metered into the petroleum which is to be tagged; since this latter step represents a very large dilution, the resulting suspension is expected to be very stable.

COSTS OF ACTIVE TAGGING

The materials cost for particle tagging should be very small. The matrix of the particles will probably be a quite common plastic or glass, and would cost a few cents to a few dollars a pound. Assuming the cost of particulate tagging material is $4.53 a pound and one milligram is added per metric ton of oil, then the per ton material cost is one thousandth of a cent per ton. The trace materials imbedded in this matrix would cost about the same but would be used in almost negligible quantities. The capital outlay for equipment is more expensive. For instance, laboratory apparatus to produce the microparticles would run in the neighborhood of $5,000. A microspectrofluorimeter with a lens system for single-particle measurements might cost $30,000; however, spectrographic analyses of the desired type may be purchased commercially for about $50 a sample. High quality microscopic equipment would be absolutely necessary; it is available for $4,000 to $20,000.

Halogenated, polynuclear aromatic hydrocarbons vary enormously in price. While many halogenated benzenes can be bought for under $4 a pound, the halogenated polynuclear compounds can be quite expensive. For example, 9-bromoanthracene costs $1,000 a pound, 2-fluoronaphthalene costs $360 a pound, but 1,3,6,8-tetrachloropyrene costs only $30 a pound. Even the most expensive of these compounds, however, goes a long way in a tagging system. Approximately 0.001 lb of tag in 50,000 tons of oil can be detected by electron-capture gas chromatography; even assuming the worst (the outrageous price of $5000 a pound for tagging material), $5 worth of tag would identify 50,000 tons of oil—so that the materials cost for tagging one ton of oil is 0.01¢. Obviously, many halogenated tags can be had for a fraction of this extreme price. Excellent electron-capture gas chromatographs can be had for $5,000 or less, so that the capital outlay for detection equipment is not a large expense.

The organometallic spectrographic standards that the National Bureau of Standards designed specifically for analysis of petroleum products are available from the Bureau for $2 a gram (roughly $900 a pound). These tags are detectable in dilutions of 10^{-5}, so that one gram of tag would identify about one ton of oil. The Bureau's spectrographic standards are exacting in the extreme, and these standards are not mass produced. By relaxing the requirements for such extreme chemical purity and increasing the production schedule, it seems probable that significant cost savings could be effected. Analytical instrumentation for spectrography is widely available commercially at prices beginning at several thousand dollars, and are standard equipment in most analytical laboratories.

Since the amount of tagging material that will be added to a ton of oil—whether the tags be particulate or liquid—is about one part in a billion, the cost of the tagging material is low per ton of oil. Costs of adding the tagging material should be in the same order of magnitude. Including all the quality control, analysis, and service, the actual cost of adding a "license plate" should be less than a few cents per ton of oil.

Feasibility studies and demonstration of the system's efficacy should be run before the operational tagging begins. However, the economics and technology are such that the tagging of oil can begin now.

TAGGING CODES

Apart from the type of material used for tagging, "codes" and "tagging profiles" will be involved in the system. Oil shipped into one port will be mixed upon unloading with oil from other tankers and hence the stored oil with its mixture of tagging codes will have its own unique tagging profile at a given time. Oil subsequently loaded onto a tanker will be re-tagged by the unique code assigned to the tanker. Thus, the re-tagged oil will have a new tagging profile whose dominant code will be that of the tanker that last tagged the oil. Thus, any oil or oil slick from a tanker will have an underlying tag noise with a superimposed tanker code. To identify the source—last jurisdiction—of the oil not only must the individual tags be identified but also the relative abundance of each tag.

When an unknown batch of oil is recovered for source identification and analysis is begun, two immediate questions arise: Is this oil spilled from a tanker? Who is the parent corporation? The first question arises because many ships, as opposed to tankers, spill oil, and the second arises because oil is within a corporate jurisdiction much longer than in a tanker jurisdiction. To speed up analysis a special tag would be used to identify all oil ever transported by tanker. Since there are a few very large oil companies, special tags could be assigned to each of the large companies, and smaller companies and independents could be grouped and given a special tag for their group. This would be in addition to the unique tag or code of tags assigned to a tanker. Thus, a quick analysis could answer the question as to whether the oil was ever shipped by tanker and which is the overall company in charge of the oil. If an independent tanker carried the oil this would be readily seen.

It would be very wise in setting up this tagging system to require each ship to tag its fuel oil at a bunkering station. This would eliminate confusion of tanker slicks and ship-fuel oil slicks.

TAGGING SYSTEM

Each oil company and each ship would have its own tagging code assigned. Depending on the system the code could be a unique tag or a code of tags. When a tanker loads an oil cargo, two taggings would take place: one by the loading station and one by the tanker.

Each tanker would have its pre-mixed and prepared code carried in sealed bottles. When loading is to begin, the coding bottle would be placed in the code metering pump and the coded fluid metered into the pipeline ahead of the pumps loading the tanker. The natural turbulence of the process would distribute the tagged material throughout the oil. Simultaneously the loading station would tag the oil with its own tag. A sample of the tagged oil would be taken for quality control and for subsequent comparisons with spills.

At each unloading the oil from the tanker would be sampled and then tagged by the shore facility. The sample would be analyzed for quality control and for the record in case of a spill claim. Tagging during unloading would cancel the tanker profile and eliminate the possibility of false claims against the tanker for oil subsequently spilled.

Tampering with the tagging system would be difficult because tagging is difficult to do except during loading and unloading in that thorough mixing is necessary. Furthermore, since a variety of tags are involved, it will be difficult to alter a batch of oil without its being obvious. Sophisticated analysis of the tags can be used to show that some of the tags are spurious. In other words, different batches of the same tag can have subtle differences that can be detected.

CONCLUSIONS

Two approaches to identifying oil spills: Passive tagging and active tagging have been examined. Passive tagging is a convenient circumlocution for no tagging at all: Nothing is added to the oil; the slick itself must provide all the evidence for its identification. Active tagging involves adding some known and readily identifiable material to the oil. The added material must satisfy several criteria: It must be soluble or dispersible in oil and insoluble and nondispersible in water; it must be chemically and physically stable in both spilled and unspilled oil; it must not interfere with the refining or with the commercial uses of petroleum; and it must not be too expensive. Two figures of speech are helpful in distinguishing active tagging from passive tagging: Passive tagging amounts to a "fingerprint," active tagging amounts to a chemical or physical "license plate."

Passive tagging does not seem promising, for the fingerprint is likely to be altered or to disappear as the slick is exposed to the abundant sources of chemical and physical energy in the sea and sky. The easily identifiable passive tags of petroleum (e.g., isotope ratios and trace metals) cannot be assumed to be stable in the slick—indeed, there is little doubt that they are unstable—and the more stable passive tags in the slick (e.g., heavy aromatic and alkylaromatic hydrocarbons) are prohibitively difficult to separate and identify.

Active tagging, however, offers several attractive possibilites: Making a good license plate seems much easier than finding a good fingerprint. Two types of tags: Oil-soluble tags (organometallics and halogenated aromatic polycycles) and particulate tags (coded microspheroids) have been examined. Several promising organometallics have been developed by the National Bureau of Standards in conjunction with the American Petroleum Institute; these compounds sell for $2 a gram, they are detectable in parts per million, and they seem to have all the properties of good active tags (compatibility with oil, solubility in water, chemical and physical stability, and ease of identification). The halogenated polycycles have never been used for analytical tracing in petroleum; consequently, no direct experience recommends them. However, they should have many desirable properties, and chemical theory recommends them. Their cost can range from a few dollars to a few thousand dollars a pound, but they are very readily detectable in parts per billion by electron-capture gas chromatography.

Although the feasibility of particulate tags has not been demonstrated in oil spills, coded microspheroids appear to have exceptional promise: Many are already commercially available at very low prices; an astronomic variety of coded microspheroids can be cheaply and easily made by custom synthesis; and all the particulate tags can be quickly separated from samples of slick and readily identified by available analytical techniques.

REFERENCES

1. DEAN RA (1969?). The chemistry of crude oils in relation to their spillage on the sea, pp. 285-289 in U.S. CONGRESS, HOUSE OF REPRESENTATIVES, COMMITTEE ON MERCHANT MARINE AND FISHERIES (1969), Hearings before the Committee, 91-1, on H.R. 6495, H.R. 6609, H.R. 6794, and H.R. 7325, bills to amend the Oil Pollution Act, 1924... Serial No. 91-4. U.S. Government Printing Office, Washington, D.C. This paper was submitted to the Committee by Vice Admiral Paul E. Trimble, Assistant Commandant of the U.S. Coast Guard, as "the best comprehensive report known to the Coast Guard on the physical and chemical changes that occur to an oil spill...."

2. BLOKKER PC (1964). Spreading and evaporation of petroleum products on water, pp. 911-919 in Verlagboek van het Vierde Internationaal Havenkongres, Antwerpen, 22-27 June 1964. Apparently published by the Koninklijke Vlaamse Ingenieursvereiniging, Antwerp, Belgium.

3. REICH L & STIVALA SS (1959). Autoxidation of Hydrocarbons and Polyolefins: Kinetics and Mechanisms. Marcel Dekker, Inc., N.Y.

4. SCOTT G (1965). Atmospheric Oxidation and Antioxidants. Elsevier Publishing Co., Amsterdam, N.Y., etc. See especially pp. 93ff.

5. ELLIS C & WELLS AA, revised and enlarged by HEYROTH FF (1941). The Chemical Action of Ultraviolet Rays. Book Department, Reinhold Publishing Corp., N.Y.

6. WOLSKY AA & CHAPMAN FW Jr. (1960). A study of an intrinsic contaminant in petroleum -- the nature of vanadium in asphaltenes. Proceedings of the American Petroleum Institute 40 (Section III):423-427.

7. DAVIS JB (1967). Petroleum Microbiology. Elsevier Publishing Co., Amsterdam, N.Y., etc.

8. Van der LINDEN AC & THIJSSE GJE (1965). The mechanisms of microbial oxidations of petroleum hydrocarbons. Advances in Enzymology and Related Subjects of Biochemistry 27:469-546.

9. KRISS AE et al. (1964). Mikrobnoye Naseleniye Mirovogo Okeana. Akademiya Nauk SSSR, Izdatel'stvo "Nauka," Moskva. See especially pp. 281-285.

10. McKENNA EF & KALLIO RE (1965). The biology of hydrocarbons. Annual Review of Microbiology 19:183-208.

11. BESTOUGEFF MA (1967). Petroleum hydrocarbons, pp. 77-108 in NAGY B & COLOMBO U [eds], Fundamental Aspects of Petroleum Geochemistry. Elsevier Publishing Co., Amsterdam, N.Y., etc.

12. WHITEHEAD WL & BREGER IA (1963). Geochemistry of petroleum, pp. 248-332 in BREGER IA [ed], Organic Geochemistry. Earth Science Series, Monograph No. 16. Symposium Publications Division, Pergamon Press, Oxford, N.Y., etc.

13. MILNER OI (1963). Analysis of Petroleum for Trace Elements. International Series of Monographs of Analytical Chemistry, Vol. 14. A Pergamon Press Book, The Macmillan Co., N.Y.

14. McCOY JW (1962). The Inorganic Analysis of Petroleum. Chemical Publishing Co., Inc., N.Y.

15. COSTANTINIDES G & ARICH G (1967). Non-hydrocarbon compounds in petroleum, pp. 109-175 in NAGY B & COLOMBO U [eds], Fundamental Aspects of Petroleum Geochemistry. Elsevier Publishing Co., Amsterdam, N.Y., etc.

16. DUNNING HN (1963). Geochemistry of organic pigments, pp. 367-430 in BREGER IA [ed], Organic Geochemistry. Earth Science Series, Monograph No. 16. Symposium Publications Division, Pergamon Press, Oxford, N.Y., etc.

17. MANSKAYA SM & DROZDOVA TV (1968). Geochemistry of Organic Substances, SHAPIRO L & BREGER [trans. and ed. from the Russian]. International Series of Monographs in Earth Sciences, Vol. 28. Pergamon Press, Oxford, N.Y., etc.

18. HODGSON GW et al. (1967). Geochemistry of porphyrins, pp. 177-259 in NAGY B & COLOMBO U [eds], Fundamental Aspects of Petroleum Geochemistry. Elsevier Publishing Co., Amsterdam, N.Y., etc.

19. FALK JE (1964). Porphyrins and Metalloporphyrins: Their General, Physical and Coordination Chemistry, and Laboratory Methods. Elsevier Publishing Co., Amsterdam, N.Y., etc.

20. JOHANNESSON JK (1955). The identification of fuel oils polluting coastal waters. The Analyst (London) 80(956):840-841.

21. CANEVARI GP (1968). A method to identify oil slicks of unknown origin. Esso Research and Engineering Co., Esso Engineering, Technology Department. Unpublished memorandum, dated 8 November 1968.

22. GUINN VP & BELLANCA SC (undated; 1968 or later). Neutron activation analysis identification of the source of oil pollution of waterways. Gulf General Atomic Inc., San Diego, California. Unpublished manuscript.

23. MARTIN DF (1968). Marine Chemistry (2 volumes). Marcel Dekker, Inc., N.Y.

24. KIRBY JG & MOORE BM (1968). Crude petroleum and petroleum products, pp. 837-947 in U.S. DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, Minerals Yearbook 1967, Volume I-II -- Metals, Minerals, and Fuels. U.S. Government Printing Office, Washington, D.C.

25. THODE HG et al. (1958). Sulphur isotope abundances in petroleum and associated materials. Bulletin of the American Association of Petroleum Geologists 42(11):2619-2641.

26. THODE HG (1963). Sulphur isotope geochemistry, pp. 25-41 in SHAW DM [ed], Studies in Analytical Geochemistry. The Royal Society of Canada, Special Publications, No. 6. University of Toronto Press, Toronto.

27. THODE HG et al. (1961). Sulphur isotope geochemistry. Geochimica et Cosmochimica Acta 25(3):159-174.

28. HARRISON AG & THODE HG (1958). Mechanism of the bacterial reduction of sulphate from isotope fractionation studies. Transactions of the Faraday Society 54(1):84-92.

29. JONES GE & STARKEY RL (1957). Fractionation of stable isotopes of sulfur by microorganisms and their role in native deposition of sulfur. Applied Microbiology 5(2):111-118.

30. SMITH HN (1968). Qualitative and quantitative aspects of crude oil composition. U.S. Department of the Interior, Bureau of Mines, Bulletin 642.

31. ABLESON PH (1967). Oil pollution. Science 156(3778):1037.

32. LUDWIG HF & CARTER (1961). Analytical characteristics of oil-tar materials on Southern California beaches. Journal of the Water Pollution Control Federation 33(11):1123-1139.

33. LUDWIG HF et al. (1964). Characteristics of oil and grease found in the marine environment. Water & Sewage Works 111(11):486-491.

34. MAPES G (1969). Troubled waters: pollution of the seas, beaches by oil poses major global problem. The Wall Street Journal 174(104):1, 20; 26 November 1969.

35. SCHULDINER JA (1951). Identification of petroleum products by chromatographic fluorescence methods. Analytical Chemistry 32(11):1676-1680.

36. AROZENA AA (1967). Contaminación del agua del mar por el petróleo. -- El paso del oxígeno atmosférico a través de capas de petróleo de distintos espesores. Ministerio de Marina, Subsecretaria de la Marine Mercante, Instituto Espanol de Oceanografía, Boletin No. 131, August 1967. El Ministerio, Madrid. [N.B. In all previous citations of this author's surname in the Boletín, the name appears as AROCENA.]

37. HERD M (1953). A paper-strip method of examining fuel oils suspected of being identical. The Analyst (London) 78(927):383-384.

38. PAULING L (1960). The Nature of the Chemical Bond, 3rd Edition. Cornell University Press, Ithaca.

39. BADGER GM (1954). The Structures and Reactions of the Aromatic Compounds. The Cambridge University Press, Cambridge, England.

40. FUSON RC (1962). Reactions of Organic Compounds: A Textbook for the Advanced Student. John Wiley & Sons, N.Y.

41. GAFNER G & HERBSTEIN FH (1960). The crystal and molecular structures of overcrowded halogenated compounds. I. Introductory survey. Acta Crystallographica 13(9):702-705.

42. LeMAIRE GW (1958). A study of structures of molecular complexes found in heavy petroleum fractions. Quarterly of the Colorado School of Mines 52 (4):1-79.

43. SERGIENKO SR (1965). High-molecular Compounds in Petroleum, SCHMORAK J [trans. from Russian]. Israel Program for Scientific Translations, Jerusalem. Daniel Davey, N.Y., U.S. Agent.

44. LOVELOCK JE & LIPSKY SR (1960). Electron affinity spectroscopy -- a new method for the identification of functional groups in chemical compounds separated by gas chromatography. Journal of the American Chemical Society 82(2):431-433.

45. MITCHELL J Jr. (1961). Gas-chromatography-detector systems, in CHERONIS ND [ed], Microchemistry Journal Symposium Series, Submicrogram Experimentation 1:201-218. Interscience Publishers, N.Y.

46. PIOZZI F & VITA-FINZI P (1960). Gascromatografia di idrocarburi fenantrenici. Atti della Accademia Nazionale dei Lincei, Serie Ottava, Rendiconti, Classe di Scienze fisiche, matematiche e naturali 29(6):549-554.

47. ROUAYHEB GM et al. (1962). Quantitative gas chromatographic analysis of hydrocarbon systems using the Lovelock diode detector and capillary columns. Analytica Chimica Acta 26(4):378-390.

48. ALBERT DK (1967). Determination of nitrogen compound types and distribution in petroleum by gas chromatography with a coulometric detector. Analytical Chemistry 39(10):1113-1117.

49. CREMER E et al. (1961). Anwendung eines hochempfindichen selektiven Halogen-Detektors in der Gas-Chromatographie. Chemie-Ingenieur-Technik 33(9):632-633.

50. SCHULEK E & REMPORT-HORVATH Zs (1960). Die Bestimmung von Halogenen in organischen Stoffen. Annales Universitatis Scientiarum Budapestinensis de Rolando Eötvös Nominatae, Sectio Chimica 2:123-128.

51. SOLO AJ & PELLETIER SW (1961). The gas-liquid chromatography of phenanthrenes; its application to the separation and identification of dehydrogenation mixtures from natural products. Chemistry & Industry 1961(43):1755-1756.

52. TUEMMLER FD (1967). Petroleum. Analytical Chemistry 39(5): 157R-190R.

53. ZLATKIS A [ed] (1969). Advances in Chromatography: Proceedings of the 5th International Symposium, 20-23 January 1969, Las Vegas, Nevada. Preston Technical Abstracts Co., Evanston, Illinois.

54. ETTRE LS (1968). Theory and applications of gas chromatography, pp. 28ff. in KROMAN HS & BENDER SR [eds], Industry and Medicine. Grune & Stratton Co., N.Y.

55. LANSDOWNE RA & LIPSKY SR (1962). Electron capture spectroscopy, an adjunct to gas chromatography. Analytical Chemistry 34(7):726-730.

56. KAWAHARA FK et al. (1968). Microanalyses of 14 chlorohydrocarbons in wastewater by thin layer and gas chromatography. Journal of Gas Chromatography 6(1):24-27.

57. ROSEN AA & MIDDELTON FM (1959). Chlorinated insecticides in surface waters. Analytical Chemistry 31(10):1729-1732.

58. SMITH JE (1961). Gas chromatographic investigations of chlorinated hydrocarbons and attendant air-sampling techniques. Ph.D. thesis, University of Colorado. Library of Congress Microfilm 61-809. Dissertation Abstracts 21(10):2871-2872.

59. SCHULTZE GR & KIRCHOFF K (1968). Analysis of petroleum and its derivatives. Erdoel, Kohle, Erdgas, Petrochemie 21(3):148-154.

60. WHITHAM BT (1959). Recent applications of gas chromatographic techniques in the petroleum industry. 31e Congrès International de Chimie, Liège, 1958. Compte Rendu [in 2 volumes], Industrie Chimique Belge, Bruxelles. Volume I, pp. 563-570. Library of Congress call number TP5.C6.

61. SCHOLLY PR & BRENNER N (1961). Comparative retention values of representative sample types on standard gas chromatography columns. 2nd International Symposium on Gas Chromatography, East Lansing, Michigan, 1959:263-309.

62. SCHOMBURG G (1968). Identification by retention and response values, KELLER RA [trans. from German]. Advances in Chromatography 6:211-245.

63. KAINZ G & WACHBERGER E (1968). Determination of chlorine traces in crude oil by combustions and potentiometric titration in nonaqueous media. Mikrochimica Acta 1968(3):596-601.

64. LARSON CM & LARSON R (1960). Additives for petroleum products, in GUTHRIE VB [ed], Petroleum Products Handbook, 1st Edition. McGraw-Hill, N.Y.

65. PINTA M (1966). Detection and Determination of Trace Elements Absorption Spectrophotometry, Emission Spectroscopy, Polarography, BIVAS M [trans. from the 1962 French edition]. Isreel Program for Scientific Translations, Jerusalem. Daniel Davey, N.Y., U.S. Agent.

66. CIUFFOLOTTI L et al. (1964). Trace metal analysis of oils and asphalts by neutron activation techniques, pp. 433-446 in COLOMBO U & HOBSON GD [eds], Advances in Organic Geochemistry. International Series of Monographs in the Earth Sciences, Monograph No. 15. Symposium Publications Division, Pergamon Press, Oxford, N.Y., etc.

67. THE AMERICAN PETROLEUM INSTITUTE (1964). Twenty-ninth midyear meeting session on activation analysis [a collection of five papers]. Proceedings of the American Petroleum Institute 44 (Section III): 233-276.

68. HENNEBERG D (1961). Eine Kombination von Gaschromatograph and Massenspektrometer zur Analyse organischer Stoffgemische. Frensenius' Zeitschrift für Analytische Chemie 183(1):12-23.

69. SIMMONS MC & KELLEY TR (1961). Quantitative analysis of complex samples by gas-liquid chromatography and mass spectrometry. 2nd International Symposium on Gas Chromatography, East Lansing, Michigan, 1959:225-236.

70. ISBELL HS et al. (1962). Analytical standards for trace metals in petroleum products. U.S. Department of Commerce, National Bureau of Standards, Monograph 54. U.S. Government Printing Office, Washington, D.C.

71. SANDERS JM (1937). The microscopical examination of crude petroleum. Journal of the Institution of Petroleum Technologists 23 (167): 525-573.

72. GREGORY PH (1961). The Microbiology of the Atmosphere. Plant Science Monographs, Leonard Hill Ltd., London, and Interscience Publishers, Inc., N.Y.

73. SKARLEW S (1934). Preparation of microscopic glass spheres. Industrial & Engineering Chemistry - Analytical Edition 6(2):152-153.

74. SOLLNER K (1939). A simplified method of preparing microscopic glass spheres. Industrial & Engineering Chemistry - Analytical Edition 11(1):48-49.

75. BLOOMQUIST CR & CLARK A (1940). Preparation of microscopic glass spheres. Industrial & Engineering Chemistry - Analytical Edition 12(1):61-62.

76. LAAN H van der & NICHOLLS RW (1960). Simple apparatus for making 10- to 100-μ spheres of low melting point metals. Review of Scientific Instruments 31(2):212.

77. POTTER CC (1966). Direct current plasma... a new spheroidizing process. Metal Progress 90(5):127-130.

78. ANONYMOUS (1961). Spheroidization of particles, ceramics, metals, refractories, and radioactive materials... [editorial information]. Industrial & Engineering Chemistry 53(2):95A.

79. McCRONE WC et al. (1967). The Particle Atlas. Ann Arbor Science Publications Inc., Ann Arbor, Michigan.

80. BLANCHARD MB (1967). Method for determining the density of microsize spherical particles. Bulletin of the Geological Society of America 78(3):385-404.

81. KIRK PL (1950). Quantitative Ultramicroanalysis. John Wiley & Sons, Inc., N.Y.

82. MEINKE WW & SCRIBNER BF (1967). Trace Characterization: chemical and physical. U.S. Department of Commerce, National Bureau of Standards, Monograph 100. U.S. Government Printing Office, Washington, D.C.

83. SVENTITSKII NS (1965). Visual Methods of Emission Spectroscopy, VARDIN P [trans. from Russian]. Israel Program for Scientific Translations, Jerusalem. Daniel Davey & Co., N.Y., U.S. agent.

84. HARVEY CE (1964). Semiquantitative Spectrochemistry. Applied Research Laboratories, Inc., Glendale, California.

85. HERCULES DM [ed] (1966). Fluorescence and Phosphorescence Analysis. Interscience Publishers, N. Y.

86. KHOMIKOVSKY P & REHBINDER P [sic] (1938). Dependence of stabilization and wetting of particles suspended in oil medium on the quantity of surface-active substances adsorbed. Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS 18(8):575-578. [In English.]

87. KOELMANS H (1955). Suspensions in non aqueous [sic] media. Doctoral thesis, University of Utrecht, The Netherlands. Special private printing, Eindhoven, The Netherlands.

88. KNOWLES EC et al. (1967). Stable suspensions of powders. U.S. Patent: US 3,328,238 (Cl. 167-16), 27 June 1967 (applied for 22 December 1965).

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Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids) have been examined. Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are satisfactory for the job; and the three types of active tags reviewed show promise and merit.

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